Semiclassical Quantization Via Classical Adiabatic Invariance of Action Variables: Stäckel Approximation for Polyatomic Molecules

S. Saini
Theoretical Atomic and Molecular Physics Group

This paper was prepared for submittal to:
Physical Review A

March 17, 1988

CIRCULATION COPY

:

DISCLAIMER

:

Semiclassical Quantization Via Classical Adiabatic Invariance of Action

Variables: Stäckel Approximation for Polyatomic Molecules[*]

PACS numbers: 03.65.Sq, 31.15+q, 33.10Cs

Subhash Saini

Theoretical Atomic and Molecular Physics Group
Lawrence Livermore National Laboratory
University of California
P.O. Box 808, Livermore
California 94550

ABSTRACT

The semiclassical method of adiabatic switching (AS) is applied to calculate highly excited vibrational energy levels of an incommensurate two dimensional coupled oscillators system. The reference Hamiltonian chosen consists of locally fitting a Hamiltonian <u>not</u> by two uncoupled harmonic oscillators but by a Stäckel Hamiltonian. At low energy this Stäckel Hamiltonian is an excellent separable approximation to the full Hamiltonian and this has been quantized for the first time. The difference between the full and the Stäckel Hamiltonian is turned on adiabatically. Results obtained by using the Stäckel Hamiltonian as a reference Hamiltonian are in excellent agreement with exact quantum variational results and are a significant improvement over the results when the reference Hamiltonian is taken to be two uncoupled oscillators. By using this Stäckel approach the computational effort to calculate the vibrational energy level is drastically reduced The Stäckel approximation to numerical potentials by local and global fitting is also discussed.

I.INTRODUCTION

Recent developments in laser spectroscopy and laser chemistry have attracted a great deal of interest in understanding the dynamics of vibrationally excited states of polyatomic molecules. This has stimulated efforts to develop methods for calculating the energy levels in the high energy region where anharmonicity is significant and modes are coupled. At present calculations are done with two general methods, viz. the exact quantum variational methods (EQ) and semiclassical (SC) methods. The EQ method is exact but becomes computationally intractable at an energy well below the dissociation energy. The accuracy and efficiency of variational methods are highly sensitive to the choice of basis functions and coordinates. The computation time for the EQ method scales as N^3 with the number of basis functions N. If in addition, the numerical integration is also required to evaluate the matrix elements, a significant portion of the total computational time may be involved in setting up the Hamiltonian matrix.

In view of the computational difficulties involved with EQ method much attention has been devoted to developing alternate methods to calculate the eigenvalues of coupled oscillators. Several methods have been developed to find the eigenvalues for two dimensional systems. The vast literature on this subject has been summarized in the two recent review articles.[1-2]

Various methods[4-25] have been developed to quantize near–integrable classical Hamiltonians. Most of these methods are based on the well known Einstein–Brillouin–Keller (EBK) quantization theory. The basic idea of adiabatic switching (AS) is due to Ehernfest.[3] Use of the adiabatic hypothesis of classical mechanics to locate trajectories with quantized values of the good actions in near–integrable systems was first proposed by Solev'ev[7] who made the first attempt to numerically implement this approach. In the past the AS method has been applied in atomic physics[9 20 25], optics[8], chemical physics[10-19] and nuclear physics.[32]

Skodje et al.[12] and Grozdanov et al.[15-16] extended and tested the AS method and demonstrated how it can be efficiently employed in problems related to chemical physics. Patterson[13] applied the AS method to a triply degenerate anharmonic oscillator– Hecht Hamiltonian suitable for octahederal and tetrahedral symmetry. Johnson[13-14] has made a systematic study to determine the best form of the switching function to maximize the rate of convergence of the energy to its adiabatic limit. The first application of AS in atomic physics was made by Grozdanov and Solev'ev[9] who calculated the first three energy levels of hydrogen atom in crossed electric and magnetic fields. The first comprehensive application of AS in atomic physics was made by Saini and Farrelly[20] who applied the AS method to calculate the energies of hydrogen atom in strong magnetic fields including the chaotic region of the phase space. Saini et al.[25] successfully applied the AS method to calculate the energy levels for the hydrogen atom in the static, uniform collinear magnetic and electric fields. The first application of AS method to calculate the vibrational energy levels for a three dimensional realistic potential applicable to SO_2 has been made by Saini et al.[24] who have also calculated the highly excited states of 3–, 4– and 5–dimensions Hamiltonians systems.

A basic problem in applying AS or self–consistent–field (SCF) methods is the choice of integrable reference Hamiltonian (usually, but not necessarily, separable) whose classical dynamics should be qualitatively as close as possible to the full Hamiltonian. The ability to apply the AS method successfully rests on being able to chose a reference zeroth order Hamiltonian in such a way as to define a good set of action variables. Whenever the potential is given in a numerical form or as a polynomial fit to experimental data it will be next to impossible to define a good set of initial quantized actions. This is the main drawback of the AS method and is a major impediment to studying a realistic molecular potentials in spite of the great success[24] in applying the AS method to SO_2 represented by a realistic potential. To overcome this problem which is fundamental not only in the AS method but also in the SCF method, we present here a new approach in defining the zeroth order reference Hamiltonian which for low energy is an excellent separable approximation for the full Hamiltonian.

In this paper we have applied a Hulst[26] method of finding a separable Hamiltonian (so called Stäckel Hamiltonian) which at the low energy is an excellent approxiamation to the full Hamiltonian. It may be mentioned that since Stäckel Hamiltonian is separable, it is integrable and its classical dynamics is regular. It is also possible to have a non–separable but integrable Hamiltonian.[20] It is well known that Hamilton–Jacobi equation is separable in a restricted number of special cases, the so called Stäckel potentials. The method used is based upon the procedure pioneered by Hulst[26] and consists of locally fitting a potential close to an equilibrium point by a Stäckel potential in elliptical coordinates instead of by a harmonic oscillator. Such a fitting is typically of significantly higher order than quadratic. Using this method Hulst[26] obtained excellent agreement with numerically calculated orbits. Recently Zeeuw and his co–workers[28-31] considered the more interesting problem of obtaining a global fit to a non–separable (and non–integrable) potential by a Stäckel potential. This procedure generates a coordinate system in which the true potential must separate. As a first step toward applying Stäckel approach in conjunction with AS method to a realistic potential in the form of numerical tables, we apply in this paper, this technique to an incommensurate two dimensional coupled oscillators system which has been studied by us previously using the AS method.

In the earlier application of the AS to an incommensurate two–dimensional coupled oscillators system[15], the reference Hamiltoinan was taken to be the two uncoupled oscillators system. In that work it was found that most of the quantizing trajectories of the full Hamiltonian are characterized by the deformed rectangular caustics and evolve adiabatically from (initial) quantized trajectories of H_0 with box–like (rectangular) caustics. Departures from this behavior were expected for quantized trajectories corresponding to the highly excited states but even at low energy the final state looks like a deformed box. This necessitated the need of finding a new reference Hamiltonian H_{ref} whose dynamics is as close as possible to the full Hamiltonian H. In other words find an integrable reference Hamiltonian

H_{ref} in such a way that the perturbation $(H - H_{ref})$ is as small as possible.

The rest of the paper is organized as follows: In Sec. II we very briefly review the AS method. In Sec. IIIA we apply the AS by taking reference Hamiltonian as two uncoupled harmonic oscillators. In Sec. IIIB we apply Hulst[26] technique of finding reference (Stäckel) Hamiltonian and use this for performing the AS. In Sec. IV we present results and discussions. Finally Sec. V contains some concluding remarks.

II. TIME DEPENDENT ADIABATIC SWITCHING METHOD

The non–integrable Hamiltonian H is first divided into a sum of two parts. i.e.

$$H(t) = H_{ref} + s(t) [H - H_{ref}] \tag{2.1}$$

where H_{ref} is an integrable but not necessarily separable zeroth order Hamiltonian. This H_{ref} should be so chosen so that its topology is as close as possible to the full Hamiltonian. [$H - H_{ref}$] is a remaining part of the Hamiltonian. $s(t)$ is an adiabatic switching function which changes slowly, smoothly and monotonically from 0 to 1 over the course of switching time T and is given by

$$s(t) = \frac{t}{T} - \frac{\text{Sin} (2 \pi t/T)}{2 \pi}, \quad 0 \leq t \leq T, \tag{2.2}$$

with the property that

$$s(t) = 0 \text{ at } t = 0 ; \quad s(t) = 1 \text{ at } t = T \tag{2.3}$$

Using the time dependent Hamiltonian given by Eq. (2.1), we integrate Hamilton's equations of motion over the time interval 0 to T for position coordinates and their conjugate momenta.

H_{ref} is quantized by imposing EBK conditions which restricts the initial values of positions and momenta to lie on invariant tori. If H_{ref} is separable then generation of initial conditions is simple and straightforward and in most cases analytical. However, if H_{ref} is not separable, then the generation of initial conditions on the zeroth order invariant in not trivial.[20] By the principle of adiabaticity at the end of switching i.e. $t = T$ the actions will remain unchanged and therefore the same EBK conditions specified at $t = 0$ will still be valid and thus the energy is quantized.

The most suitable reference Hamiltonian is the one whose topology is as close as possible to the full Hamiltonian. Thus the AS method requires deep insight of the classical dynamics of the problem. If Hamiltonian is integrable but not separable one also need to know the quantities which are approximately conserved for the full Hamiltonian. If the system is degenerate then the number of single–valued integrals of motion is greater than the number of degrees of freedom. In that event, the set of EBK quantization conditions cannot be chosen in a unique way. In fact, they have been reduced. Thus there is a need to lift degeneracy in the reference Hamiltonian. This is analogous to degenerate quantum system where more than one eigenfunction corresponds to a particular eigenvalue.

III. MATHEMATICAL FORMULATION

In this section we apply the AS method to study the model molecular Hamiltonain system by using, (a) two uncoupled harmonic oscillators system as a reference Hamiltonian, and (b) using the Stäckel Hamiltonian as a reference Hamiltonian. We will discuss these cases separately.

A Adiabatic Switching Using Two Harmonic Oscillators as Reference Hamiltonian

The molecular Hamiltonian studied by us is given by

$$H = \frac{1}{2}\left[p_x^2 + p_y^2 \right] + \frac{1}{2}\left[\omega_x^2 x^2 + \omega_y^2 y^2 \right] - \left[\frac{a}{3}\right] x \left[x^2 + (3b/a)\, y^2 \right] \qquad (3.1)$$

with

$$\omega_x = 0.7, \quad \omega_y = 1.3, \quad ; a = 0.03, \quad b = 0.1 \ . \qquad (3.2)$$

The reference Hamiltonian used is a two uncoupled harmonic oscillator Hamiltonian and is given by

$$H_o = 1/2 \left[\left[p_x^2 + \omega_x^2 x^2 \right] + \left[p_y^2 + \omega_y^2 y^2 \right] \right] \qquad (3.3)$$

For the AS we have

$$H(t) = H_o + s(t) \left[H - H_o \right] \qquad (3.4)$$

The initial conditions sampling the reference Hamiltonian H_o are

$$x^o,\, y^o = \left[\frac{2\, I_{x,y}}{\omega_{x,y}} \right]^{1/2} Sin\left[\theta_{x,y}^o \right] \qquad (3.5)$$

$$p_{x,y}^o = \left[2 I_{x,y}\, \omega_{x,y} \right]^{1/2} Cos\left[\theta_{x,y}^o \right] \qquad (3.6)$$

where the quantized action variables are given by

$$I_{x,y} = n_{x,y} + 1/2, \qquad n_{x,y} = 0,\, 1,\, 2,\, ... \qquad (3.7)$$

and the angle variables are given by $0 \leq \theta_{x,y}^o < 2\pi$

B Adiabatic Switching Using Stäckel Hamiltonian as Reference Hamiltonian

In this section we will apply the technique pioneered by Hulst[26] to find the separable approximation to the full non–integrable Hamiltonian to calculate the time periods of the planets. Since this technique is described in the astronomical literature[26], is therefore likely it may be somewhat unfamiliar to the community of molecular physics. For this reason coupled with the fact that the journal in which this technique appeared has gone out of publication we outline the details of the method.

Let us define the elliptical coordinates ξ and η defined by

$$x = c \, \text{Sinh}(\xi) \, \text{Cos}(\eta) - k, \qquad (3.8a)$$

$$y = c \, \text{Cosh}(\xi) \, \text{Sin}(\eta) \qquad (3.8b)$$

where $x = -k$ and $y = \pm c$ define the position of the two foci. Along ξ or η the local scale is given by

$$\left[\frac{ds}{d\xi}\right]^2 = \left[\frac{ds}{d\eta}\right]^2 = R = c^2 \left(\text{Cosh}^2\xi - \text{Sin}^2\eta \right) \qquad (3.9)$$

The angle ϵ by which either of the coordinate curves are rotated in x and y directions is given by the following equation

$$\tan(\epsilon) = \tanh(\xi) \, \tan(\eta) \qquad (3.10)$$

Let us introduce the following quantities

$$x_0 = c \, \text{Sinh}(\xi) - k, \, , \tag{3.11a}$$

$$R_0 = c^2 \, \text{Cosh}^2(\xi) \tag{3.11b}$$

$$= \ell^2 + 2k \, x_0 + x_0^2$$

$$\ell^2 = c^2 + k^2 \tag{3.11c}$$

If we expand in powers of η and retain the terms only up to quadratic in η, then Eqs. (3.8) – (3.11) can be written as

$$x = x_0 - 1/2(k + x_0)\eta^2, \tag{3.12a}$$

$$y = R_0^{1/2}\eta \tag{3.12b}$$

$$R = R_0 - c^2 \, \eta^2, \quad . \tag{3.12c}$$

$$\tan \epsilon = (k + x_0) \, \eta \, R_0^{1/2} . \tag{3.12d}$$

If E is the total energy and V(x,y) the potential energy then separation of variables is possible if R and RV respectively are functions of ζ and η and we get

$$2R = \kappa(\xi) + \lambda(\eta), \tag{3.13a}$$

$$2R \, V = -[\, \mu(\xi) + \nu(\eta) \,] \tag{3.13b}$$

From Eq. (3.1) the total potential is given by

$$V(x,y) = 1/2 \left[\omega_x^2 x^2 + \omega_y^2 y^2 \right] - \frac{a}{3}x^3 - b \, x \, y^2 + ... \tag{3.14}$$

where the dots stand for terms of the higher order in x and/or y^2. We calculate the value of of c and k in such a way that Eq. (3.13) is satisfied as closely as possible giving us an approximation which is accurate for small amplitudes. Using Eqs. (3.12) and (3.14) we get

$$2R\ V = \delta_1(x_o) + \eta^2\ \delta_2(x_o) \tag{3.15}$$

where

$$\delta_1(x_o) = -\mu(\xi) = R_o \left[\omega_x^2\ x^2 - \frac{2a}{3}\ x_o^3 \right] + \ .. \tag{3.16a}$$

$$\delta_2(x_o) = -\eta^{-2}\ \mu(\eta) = R_o^2 \left[\omega_y^2 - 2b\ x_o \right] - c^2 \left[\omega_x^2\ x_o - \frac{2a}{3}\ x_o^3 \right]$$

$$\doteq R_o \left[\omega_x^2\ x_o(k + x_o) - a\ x_o^2(k + x_o) \right] \tag{3.16b}$$

$\mu(\eta)$ can be a function of η alone if $\delta_2(x_o)$ is a constant which means that at least the coefficients of x_o and x_o^2 in the Eq. (3.16a) are zero. On simplification we get

$$k \left[4\ \omega_y^2 - \omega_x^2 \right] - 2\ b\ell^2 = 0, \tag{3.17a}$$

$$\tag{3.17b}$$

$$k^2 \left[4\ \omega_y^2 - \omega_x^2 \right] + 2\ \ell^2 \left[\omega_y^2 - \omega_x^2 \right] - k\ \ell^2(\ 8b - a\ ) = 0,$$

These are two equations in two unknowns k and ℓ^2 and thus can be solved for them and we get

$$k = \frac{2 \left[\omega_y^2 - \omega_x^2 \right]}{(6b - a)} \tag{3.18a}$$

$$\ell^2 = \frac{\left[4\ \omega_y^2 - \omega_x^2 \right] \left[\omega_y^2 - \omega_x^2 \right]}{b\ (6b - a)}, \tag{3.18b}$$

with $\qquad c^2 = \left[\ell^2 - k^2 \right]^{1/2} \tag{3.18c}$

It can be easily seen that the general form of the potential $V(x,y)$ which satisfy the condition of separability exactly and which has the expansion given by Eq. (3.14) is

$$2V = \frac{2V_o R_o + \omega_y^2 \ell^4 \varphi(\eta)}{R_o - c^2 \sin^2(\eta)} \tag{3.19a}$$

$$= \frac{f_1(\xi) + f_2(\eta)}{\xi^2 + \eta^2} \tag{3.19b}$$

where R_o is the function of x_o specified by Eq. (3.11). $2V_o = \omega_x^2 x_o^2 - (2a/3) x_o^3 +$ higher order terms in x_o, and $\varphi(\eta) = \eta^2 +$ higher order terms in η^2. In this work we also assume that $\varphi(\eta) = \sin^2(\eta)$ and in $2V_o$ neglect all the terms beyond third order to get

$$\kappa(\xi) = 2 R_o ; \qquad \mu(\xi) = -2 R_o V_o, \tag{3.20a}$$

$$\lambda(\eta) = -2 c^2 \sin^2(\eta) ; \quad \nu(\eta) = -\omega_y^2 \ell^4 \sin^2(\eta), \tag{3.20b}$$

Therefore the reference Hamiltonian which we use for the adiabatic switching is given by

$$H_s = 1/2 \left[p_x^2 + p_y^2 \right]' + \frac{2 V_o R_o + w_y^2 \ell^4 \varphi(\eta)}{R_o - c^2 \sin^2(\eta)} \tag{3.21}$$

Reference Hamiltonian given by Eq. (3.21) is called Stäckel Hamiltonian and it is separable in ξ and η and is at very low energy an excellent separable approximation to the full Hamiltonian given by Eq. (3.1).

Using the reference Hamiltonian given by Eq. (3.21) we apply the AS method on the following Hamiltonian.

$$H(t) = H_{stackel} + s(t) \left[H_{full} - H_{stackel} \right] \qquad (3.22a)$$

$$H(t) = H_s + s(t) (H - H_s) \qquad (3.22b)$$

C Quantization of Stäckel Actions J_ξ and J_η

The generalized canonical momenta conjugate to position coordinates ξ and η are given as:

$$P_\xi = \left[\mu(\xi) + \kappa(\xi) E - \beta \right]^{1/2} \qquad (3.23a)$$

$$P_\eta = \left[\nu(\eta) + \lambda(\eta) E + \beta \right]^{1/2} \qquad (3.23b)$$

where β is a separation constant and is obtained iteratively.

The quantization conditions are given as

$$J_\xi(E,\beta) = 2 \int_{\xi_1}^{\xi_2} P_\xi \, d\xi = (n_\xi + 1/2), \quad n_\xi = 0, 1, 2, ..., \qquad (3.24a)$$

where ξ_1 and ξ_2 are the classical turning points and are obtained as the roots of $[\mu(\xi) + \kappa(\xi) E - \beta] = 0$.

$$J_\eta(E,\beta) = 2 \int_{\eta_1}^{\eta_2} P_\eta \, d\eta = (n_\eta + 1/2) \quad n_\eta = 0, 1, 2, ... \qquad (3.24b)$$

-13-

where η_1 and η_2 are the classical turning points and are obtained as the roots of $[\ \nu\ (\eta) + \kappa$ $(\eta)\ E + \beta\ ] = 0$. It is very easy to show that the mean periods T_ξ and T_η for small amplitudes are given by

$$T_\xi = \frac{2\pi}{\omega_x} \tag{3.25a}$$

$$T_\eta = \frac{2\pi}{\omega_y} \tag{3.25b}$$

Thus we see that for small amplitudes the time periods of H_o and H_s are the same.

IV RESULTS AND DISCUSSIONS

The AS results for the energy spectrum up to classical escape energy at $E = 11.4601$ is given in Table I. The AS results have been obtained by using two different reference Hamiltonians namely, H_o and H_s given respectively by Eqs. (3.3) and (3.21). H_o is just two uncoupled harmonic oscillators in Cartesian coordinates whereas H_s is the Stäckel Hamiltonian and is an excellent separable approximation for the full Hamiltonian at low energy. Initial conditions corresponding to H_o and H_s are generated and then the difference of $[\ H(t) - H_o\ ]$ and $[\ H(t) - H_s\ ]$ is turned on adiabatically. Each energy level is the result of 10 trajectories in the case of AS1 [using H_o as reference Hamiltonian] and 2 trajectories in case of AS2 [using H_s as a reference Hamiltonian]. In both the cases the switching function used is given by Eq. (2.2) and Hamilton's equations were integrated for T= 400. It is clearly seen from the Table I that the results obtained by AS2 are in better agreement with the exact quantum (EQ) and the standard deviations are an order of magnitude smaller as compared to that of AS1. In fact the AS2 results can be obtained to the same accuracy even with a single trajectory. This means that computational effort involved with AS2 method is 1/10 of the AS1 method.

For each eigenvalue shown in Table I we have run a few representative "final" quantized trajectories. These trajectories are obtained in the following manner. After the AS is complete (i.e. the perturbation is fully turned on) the equations of motion continue to be integrated with $s(t) = 1$ for all subsequent times $t > T$. This is equivalent to integrating Hamilton's equations for the full Hamiltonian using the initial conditions (the values of positions and momenta) obtained at the end of adiabatic switching i.e. at $t = T$. Here the term "quantizing" should be understood in a very restricted manner in the sense of approximate adiabatic invariance i.e these trajectories are not exactly quantized but are very close to them. Most of the energy levels corresponding to Table I are characterized by trajectories whose rectangular caustics have been deformed. A typical example is shown in Fig. 1. Figs. 1(a), 2(a), ..., 8(a) correspond to initial quantized trajectories corresponding to H_o [Eq. (3.3)] with initial conditions given by Eqs. (3.5) and (3.6). Figs. 1(b), 2(b), ..., 8(b) refers to initial quantized trajectories corresponding to H_s [Eq. (3.21)] with initial conditions gotten from Eqs. (3.23) and (3.24). Figs. 1(c), 2(c), ..., 8(c) refer to the quantized trajectories obtained at the end of adiabatic switching i.e. for the full Hamiltonian at $t = T$. The reason for getting better energy levels by AS2 method with two trajectories and corresponding very small standard deviations is obvious on comparing the caustics in Fig. 1. The topology of the quantized trajectory corresponding to the full Hamiltonian shown in Fig. 1(c) is much closer to the topology corresponding to H_s shown in Fig. 1(b) than to the topology of H_o shown in Fig. 1(a). The same trend is clearly seen in all the Figs. (2–7). The trajectory shown in Fig. 1(c) during its adiabatic evolution infinitely often passed through the weak classical resonance zone (CRZ) but ended outside it at $t = T$. We also found quantizing trajectories affected by weak resonances which ended inside the CRZ. This is depicted in Fig. 2(c). In this figure the trajectory is close to a periodic orbit which would have been the case if exact resonant conditions were met and lies inside the CRZ. Initial quantizing trajectories corresponding to H_o and H_s are shown in Figs. 2(a) and 2(b) respectively. If we compare Fig. 2(a) with Fig. 2(c) one can immediately see that the topology of the adiabatical torus (from H_o) has been

deformed to a great extent. However, on comparing Fig. (2b) with (2c) one finds that the topology of the initial torus (H_s) is almost the same as the final quantized state and thus the AS method gives better energy with a small standard deviation. A more pronounced effect of the (still relatively weak) resonance is shown in Fig. 3(c) – a final quantized trajectory corresponding to energy level 42. Here the change in topology is obvious and caustics are no longer a rectangular (i.e. a box) and that is why box quantization (Cartesian actions) with H_0 as the reference Hamiltonian no longer gives good results. In this case no method based upon box quantization can quantize states characterized by the trajectories shown in Fig. 3(c). For this reason semiclassical quantization of Birkhoff–Gustavson–Normal–Form (BGNF) also gives poor results. However, if we use Stäckel quantization (i.e. chose reference Hamiltonian to be H_s) we get better results as the topology of final quantized trajectory (at t = T) shown in Fig. 3(c) is almost the same as that of H_s shown in Fig. 3(b). For some of the energy levels presented in Table I the corresponding final quantized trajectories are characterized by strongly deformed rectangular caustics. A representative of such trajectories is shown in Fig. 4(c) and corresponding initially quantized trajectories obtained by H_0 and H_s respectively are shown in Figs. 4(a) and 4(b). Again one finds that the topology of final quantized trajectory [Fig. 4(c)] is closer to H_s [Fig. 4(b)] than to H_0 [Fig. 4(a)]. Many of the states (e.g. 79, 80 and 84) with mild chaotic dynamics have also been observed. A typical example of which is shown in Fig. 5(c) which has symptoms of mild chaos and will become more chaotic if run for a longer time. We get still meaningful energy levels because of the existence of the approximate adiabatic invariant corresponding to a "vague" torus – a term coined by Reinhardt.[33] Here adiabaticity has been violated. This is also reflected in the large standard deviations obtained if we use box quantization. The reason is that the topology of final quantized trajectory is entirely different from the one obtained by H_0. However, if we use H_s as the reference Hamiltonian, the results are in good agreement with the EQ with a smaller standard deviation.

States 81 and 82 are characterized by final quantized trajectories with horseshoe shaped caustics as shown in Fig. 6(c). Caustics with such trajectories are typical of a 1:2 resonance (Fermi resonance). Thus it is obvious that in the course of adiabatic switching the tori passed through the separatrix and changed topology and at $t = T$ it ended inside the CRZ exhibiting Fermi resonance and thereby its adiabaticity has been violated. We note that these states (81 and 82) are nearly degenerate states. The violation of adiabaticity is also reflected in the large standard deviation for these two states and an inversion of ordering energy levels is obtained when compared to the perturbation results of BGNF.

The last two states 84 and 85 shown in Table I have eigenvalues which lie above the the classical escape energy 11.4601. Quantizing trajectories corresponding to these states are shown in Figs. 7(c) and 8(c). Both these trajectories have been affected by some higher order resonance. Notice that quantizing trajectory of Fig. 7(c) looks similar to that of Fig. 5(c) in the sense that both trajectories show characteristics of mild chaos. However, the standard deviation corresponding to the state of Fig. 7(c) is much smaller as compared to the state of Fig. 5(c). The reason for this is that the quantized trajectory corresponding to Fig. 7(c) is located in a thin chaotic layer associated with a higher order CRZ which occupies a much smaller volume in phase space than the one associated with a low order CRZ in which a trajectory of the type shown in Fig. 5(c) lies. As a result of this during adiabatic evolution a state of the type shown in Fig. 5(c) has spent much more time in a region of phase space where the dynamics is chaotic. Therefore, violation of adiabaticity is more severe for the states of the type shown in Fig. 5(c) than for those shown in Fig. 7(c). This is reflected in the larger standard deviations in the former.

V CONCLUDING REMARKS

A fundamental problem in applying the either AS or SCF methods is the choice of coordinates in which it is most appropriate to approximately separate the problem. The

Stäckel fitting method presented in this paper can be used to define the curvilinear coordinate system in which the problem most nearly separates and then these coordinates be used in the AS and SCF methods. As an illustration of Stäckel fitting we have successfully quantized a non–degenerate two dimensional coupled oscillators system. This has been achieved by first deriving a Stäckel Hamiltonian (which is separable and hence integrable thus having regular classical dynamics) which at low energy is an excellent separable approximation to the full Hamiltonian. Then the Stäckel Hamiltonian is quantized and initial conditions are generated for this Hamiltonian. We then turn on the difference between the full Hamiltonian and the Stäckel Hamiltonian as an adiabatic perturbation. The main advantage of this Stäckel approach is that virtually with a single trajectory we get very accurate energy levels. The attraction of the AS method is that it is easy to obtain quantized trajectories irrespective of the dimensionality of the problem. No initial searches, iterative procedures, Fourier analysis, or perturbation expansions are required.

In our opinion the combination of Stäckel fitting and AS promises to be a very effective way of treating realistic molecular potentials. Investigations along this line for vibration–rotation (VR) interactions in triatomic and polyatomic molecules are being studied. An important problem in understanding VR interactions is the calculation of VR energies. For highly excited states the EQ methods become intractable. The EBK based trajectory methods also are not feasible for polyatomic molecules as they completely break down in the chaotic region in spite of the great success in applying the AS method to SO_2 (with a realistic polynomial potential). However, it does break down for H_2O and O_3 which have the same analytical form of the potential as SO_2 but are resonant, if the reference Hamiltonian is chosen to be three uncoupled harmonic oscillators. It has been shown in many studies on both model and realistic molecular Hamiltonian systems as well as more recently in quadratic Zeeman effect[20] and hydrogen atom in parallel electric and magnetic fields that the AS method works even in the mild chaotic region of the phase space. In view of this we believe that the Stäckel procedure in conjunction with AS is an efficient way of evaluating

energies of polyatomic molecules where potentials are in the form of numerical tables or piecewise analytic fits to experimental data. It may be pointed out that the present Stäckel procedure of finding the reference Hamiltonian is only applicable to two coupled incommensurate oscillators systems. For the important case of Henon–Helies (1:1) and Fermi resonance (2:1) work is in progress. We are also extending the Stäckel procedure to incommensurate three dimensional coupled oscillators system.

ACKNOWLEDGEMENT

REFERENCES

1. D. W. Noid, M.L. Koszykowski and R.A. Marcus, Ann. Rev. Phys. Chem, 32, 267 (1981).

2. W. P. Reinhardt, The Mathematical Analysis of Physical Systems, Ed. R. Mickens (Van Norstrand Reinhold, New York 1985.

3. P. Ehrenfest, Versl. Kon. Akak. Amsterdam, 25, 412 (1916). English translation in Sources of Quantum Mechanics. edited by B.L. Vander Waeden (Dover, New 1967).

4. S. Saini, K. Stefanski, G, Hose, and H.S. Taylor, Chem. Phys. Lett. 116, 35 (1985).

5. S. Saini, Chem . Phys. Lett. 125, 194 (1986).

6. T.P. Grozdanov, S. Saini, and H.S. Taylor, J. Phys. B19, 691 (1986).

7. E. A. Solov'ev, Sov. Phys. JETP, 48, 635 (1978).

8. A. Barthelemy and J. Arnaud, J. Opt. Soc. Am. 71, 32 (1981).

9 T. P. Grozdanov and E.A. Solov'ev, J. Phys. B15, 1195, (1982).

10. R. M. Hedge, R.T. Skodje, F. Borondo and W.P. Reinhardt, Am. Chem. Soc. Symp. Ser. No. 263, 323 (1984)

11. B.R. Johnson (The Aerospace Coroporation, El. Segundo, California, preprint 1984).

12. R.T. Skodje , F. Borondo and W.P. Reinhardt, J. Chem. Phys. 82, 4611 (1985)

13. C. W. Patterson, J. Chem Phys. 83. 4618 (1985).

14. B. R. Johnson, J. Chem. Phys. 83, 1204 (1985).

15. T. P. Grozdanov, S. Saini, and H. S. Taylor, Phys. Rev. A33, 55 (1986).

16. T. P. Grozdanov, S. Saini, and H. S. Taylor, J. Chem. Phys. 84, 3243 (1986).

17. C. Jaffe. J. Chem. Phys. 85, 2885 (1986).

18. J. W. Zwanziger, E. R. Grant and G. S. Ezra. J. Chem. Phys. 84, 3243 (1986).

19 C. W. Patterson, R. Scott, and R. B. Shirt, J. Chem. Phys. 85, 3341 (1986).

20 S. Saini and D. Farrelly, Phys. Rev. **A36**, 3556 (1987).

21. S. Saini and D. Farrelly, unpublished 1987.

22. B. R. Johnson, J. Chem. Phys. **86**, 1445 (1987).

23. S. Saini, J. Zakrzewski, and H. S. Taylor, Phys. Rev. **A** (submitted, 1988).

24. S. Saini, J. Zakrzewski, and H. S. Taylor, Phys. Rev. **A** (submitted, 1988).

25. S. Saini, Phys. Rev. **A** (to be submitted).

26. H. C. Van de Hulst, Bull. Astr. Inst. Netherlands, **16**, 235 (1962).

27. A. Ollongern, Bull. Astr. Inst. Netherlands, **16**, 241 (1962).

28. T. deZeeuw and D. Lyndn-Bell, Mon. Not. Roy. Astr. Soc. **215**, 713 (1985).

29. T. deZeeuw, Mon. Not. Roy. Soc., **215**, 731 (1985).

30. T. deZeeuw, Mon. Not. Roy. soc., **216**, 273 (1985).

31. T. deZeeuw, Mon. Not. Roy. Soc., **216**, 599 (1985).

32. R. Arieu, F. Brunt, J. Carbonell and J. Touchard, Phys. Rev., **A35**, 2389 (1987).

33. R. B. Shirts and W. P. Reinhardt, J. Chem. Phys. **77**, 5204 (1982).

34. R. T. Swimm and J. B. Delos, J. Chem. Phys. **71**, 1706, (1979).

TABLE I   Energy levels of the Hamiltonian defined by Eq. (2.1).

state	$(n_x\ n_y)^a$	E_o	AS1	SD1	EQ	E_s	AS2	SD2	BGNF
36	(10,0)	8.0	7.7484	1.4(-3)	7.7423	7.7605	7.7417	2.4(-5)	7.7445
37	(1,5)	8.2	7.8983	0.7(-3)	7.8996	8.0063	7.8996	2.0(-5)	7.9019
38	(3,4)	8.3	7.9505	0.9(-3)	7.9524	8.0628	7.9525	3.2(-5)	7.9564
39	(5,3)	8.4	8.0024	1.3(-3)	8.0259	8.1277	8.0259	2.0(-5)	8.0315
40	(7,2)	8.5	8.1194	0.9(-3)	8.1220	8.2064	8.1219	5.0(-5)	8.1288
41	(9,1)	8.6	8.2405	0.8(-3)	8.2435	8.3022	8.2431	0.1(-5)	8.2500
42	(11,0)	8.7	8.3902	1.0(-3)	8.3939	8.4163	8.3930	2.9(-5)	8.3973
74	(4,6)	11.6	10.8626	2.5(-3)	10.8657	11.1383	10.8662	3.3(-4)	10.8933
75	(6,5)	11.7	10.9022	1.7(-3)	10.9053	11.1190	10.9059	8.7(-5)	10.9434
76	(15,0)	11.5	10.9336	1.8(-3)	10.9439	10.9963	10.9404	6.2(-4)	10.9627
77	(8,4)	11.8	10.9658	2.2(-3)	10.9700	11.4297	10.9703	2.8(-4)	11.0172
78	(10,3)	11.9	11.0588	1.6(-3)	11.0612	11.3211	11.0602	2.5(-3)	11.1166
79	(12,2)	12.0	11.1802	7.1(-3)	11.1856	11.4074	11.1882	4.0(-3)	11.2439
80	(14,1)	12.1	11.3376	1.1(-2)	11.3484	11.5102	11.3198	1.9(-2)	11.4014
81	(1,8)	12.1	11.4149	4.8(-3)	11.4129	11.6553	11.4179	7.5(-3)	11.4369
82	(3,7)	12.2	11.4057	1.1(-2)	11.4158	11.7131	11.4110	5.2(-3)	11.4460
83	(5 6)	12.3	11.4294	3.6(-3)	11.4325	11.7634	11.4321	1.1(-3)	11.4765
84	(7,5)	12.4	11.4651	1.1(-3)	11.4703	11.8152	11.4714	1.4(-3)	11.5305
85	(16,0)	12.2	11.5519	1.8(-3)	11.5324	11.6296	11.5572	7.0(-4)	11.5902

E_0 = Energy of reference Hamiltonian Eq. (2.1).

AS1 = Semiclassical AS energy level using H_0 as reference Hamiltonian.

SD1 = Standard deviation for 10 trajectories corresponding to AS1.

EQ = Exact quantum variational results.

E_S = Energy of reference Hamiltonian H_S, Eq. (3.21), called Stäckel energy.

AS2 = Semiclassical AS energy using H_S, Eq. (3.21), as a reference Hamiltonian.

SD2 = Standard deviation for two trajectories corresponding to AS2.

BGNF= Energy level obtained from classical perturbation theory, ref. 34.

[a]The quantum numbers n_x and n_y are identical to n_ξ and n_η .

FIGURE CAPTIONS

Fig. 1. (a) Initial quantized trajectory for H_O [Eq. (3.3)]. Here $n_x = 1$, $n_y = 5$ and $E = 8.2$;

(b) Initial quantized trajectory for H_S [Eq. (3.21)]. Here $n_\zeta = 1$, $n_\eta = 5$, and $E_S = 8.0063$;

(c) Initial quantized trajectory for the full Hamiltonian H [Eq. (3.1)]. Here $n_\zeta = 1$, $n_\eta = 5$.

Fig. 2. (a) Same as Fig. 1(a) but with $n_x = 3$, $n_y = 4$, and $E_O = 8.3$;

(b) Same as Fig. 1(b) but with $n_\zeta = 3$, $n_\eta = 4$, and $E_S = 8.0828$;

(c) Quantizing trajectory within some higher order resonance. Here $n_\zeta = 3$, $n_\eta = 4$.

Fig. 3. (a) Same as in Fig. 1(a) but with $n_x = 11$, $n_y = 0$, and $E_O = 8.7$;

(b) Same as in Fig. 1(b) but with $n_\zeta = 11$, $n_\eta = 0$, and $E_S = 8.4163$;

(c) Same as in Fig. 2(c) except the order of resonance is lower. Here $n_\zeta = 11$, $n_\eta = 0$.

Fig. 4. (a) Same as in Fig. 1(a) but with $n_x = 4$, $n_y = 6$, and $E_O = 11.6$;

(b) Same as in Fig. 1(b) but with $n_\zeta = 4$, $n_\eta = 6$, and $E_S = 11.1383$;

(c) Same as in Fig. 2(c) except the order of resonance is lower. Here $n_\zeta = 4$, $n_\eta = 6$.

Fig. 5. (a) Same as in Fig. 1(a) but with $n_x = 14$, $n_y = 1$, $E_O = 12.1$;

(b) Same as in Fig. 1(b) but with $n_\zeta = 14$, $n_\eta = 1$, and $E_S = 11.5102$;

(c) Irregular quantizing trajectory with apparent chaotic characteristics. Here $n_\zeta = 14$, $n_\eta = 1$.

Fig. 6. (a) Same as in Fig. 1(a) but with $n_x = 1$, $n_y = 8$, and $E_O = 12.1$;

(b) Same as in Fig. 1(b) but with $n_\zeta = 1$, $n_\eta = 8$, and $E_S = 11.6553$;

(c) Quantizing trajectory within 1:2 classical resonance zone. Here n_ζ

$= 1$, $n_\eta = 8$.

Fig. 7. (a) Same as in Fig. 1(a) but with $n_x = 7$, $n_y = 5$, and $E_o = 12.4$;

  (b) Same as in Fig. 1(b) but with $n_\zeta = 7$, $n_\eta = 5$, and $E_s = 11.8152$;

  (c) Quantizing trajectory within 1:2 resonance zone. Here $n_\zeta = 7$, $n_\eta = 5$.

Fig. 8. (a) Same as in Fig. 1(a) but with $n_x = 16$, $n_y = 0$, and $E_o = 12.2$;

  (b) Same as in Fig. 1(b) but with $n_\zeta = 16$, $n_\eta = 0$, and $E_s = 11.6296$;

  (c) Same as Fig. 7(c) but with $n_\zeta = 7$, $n_\eta = 8$.

Figure 1

Figure.2

(a)   (b)   (c)
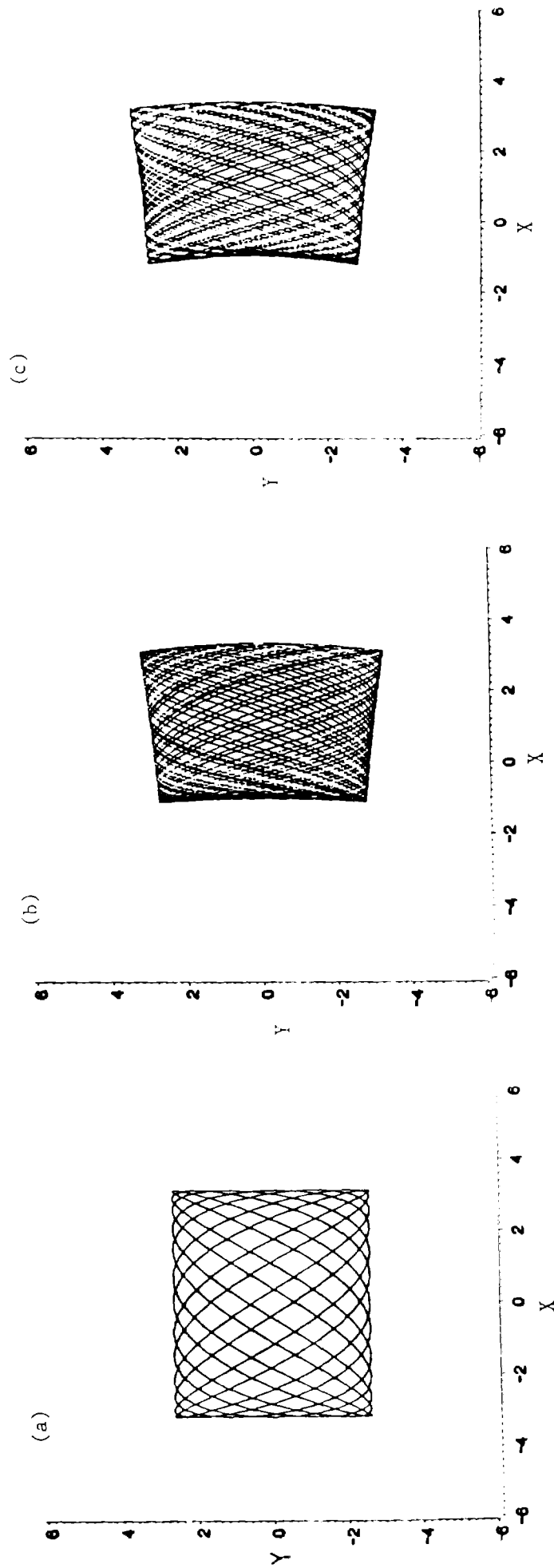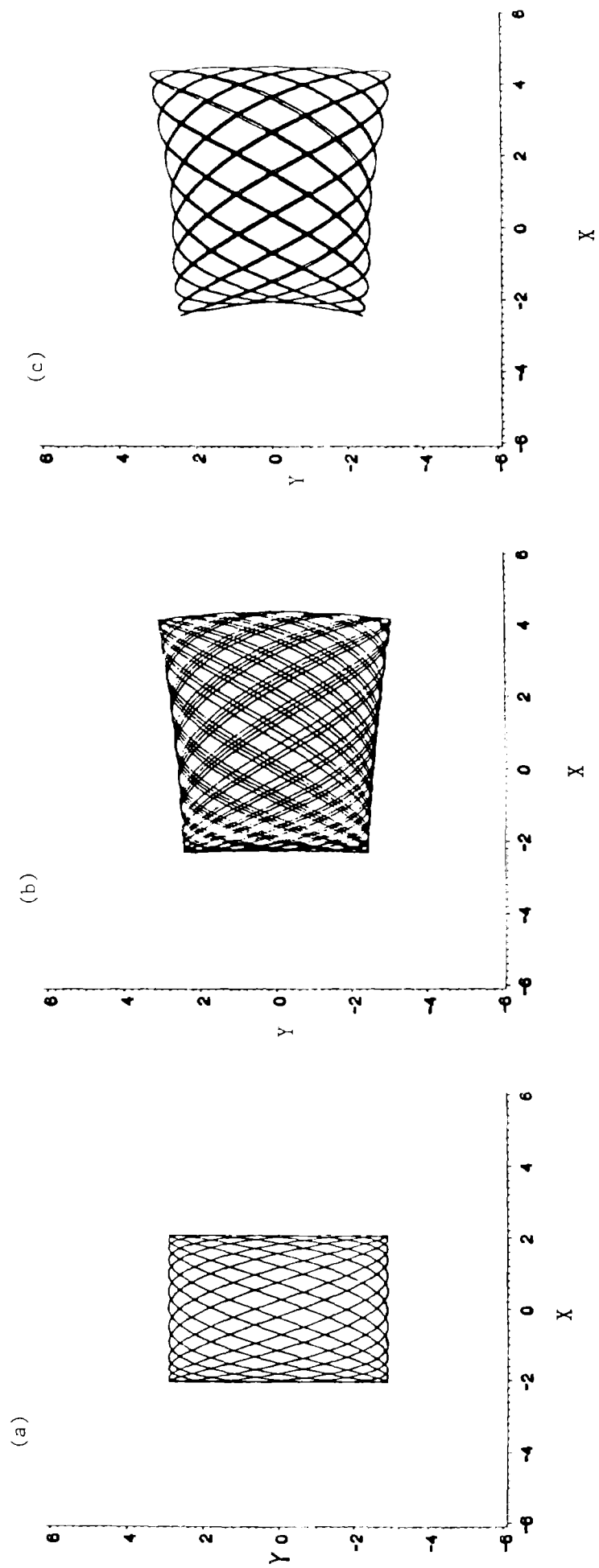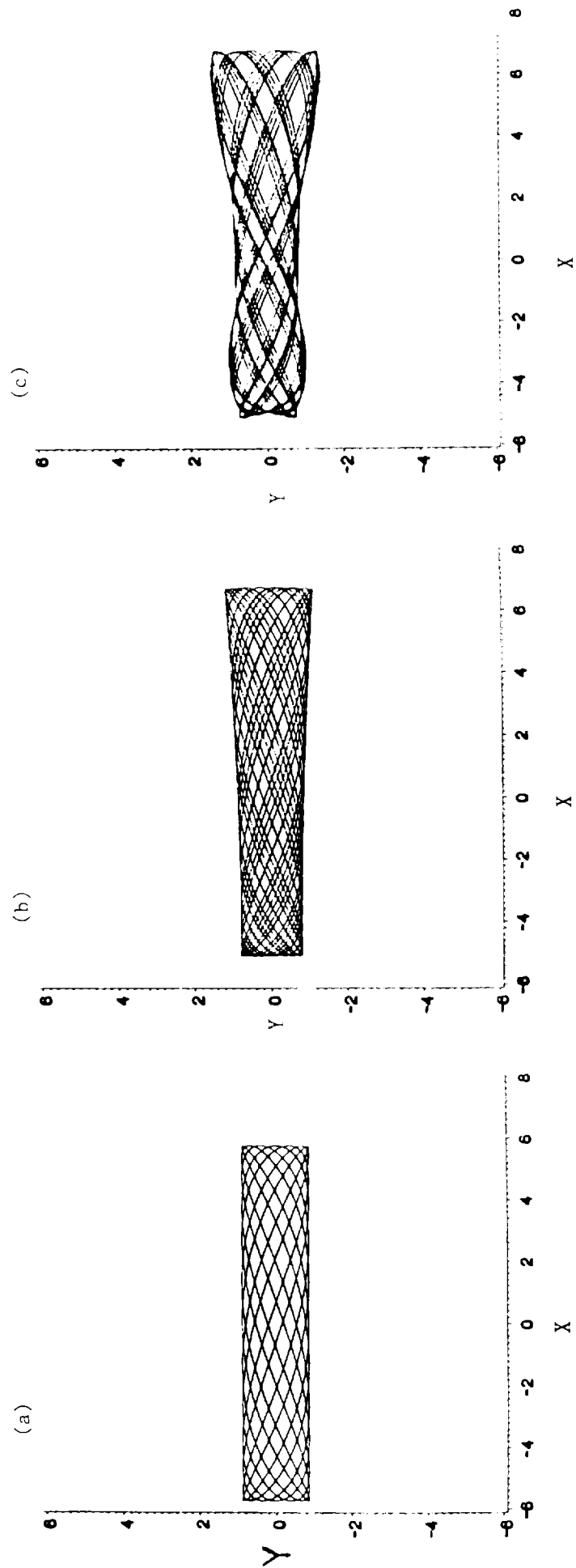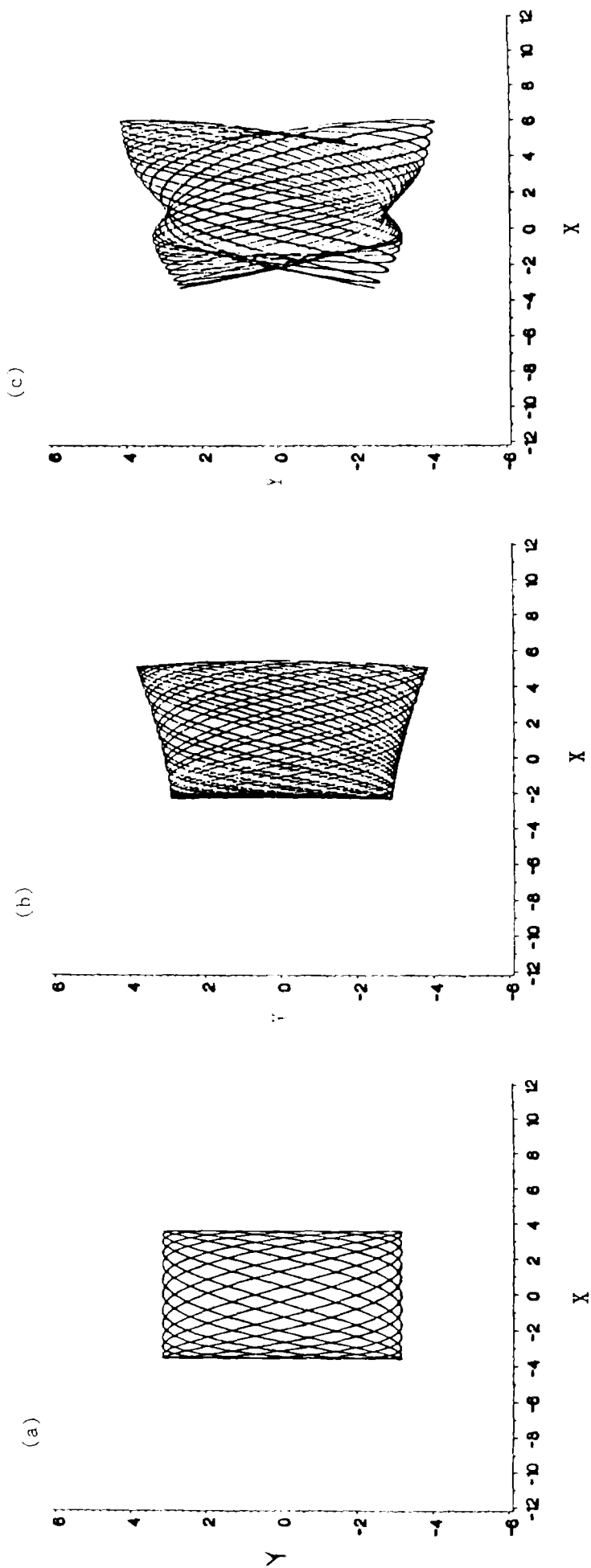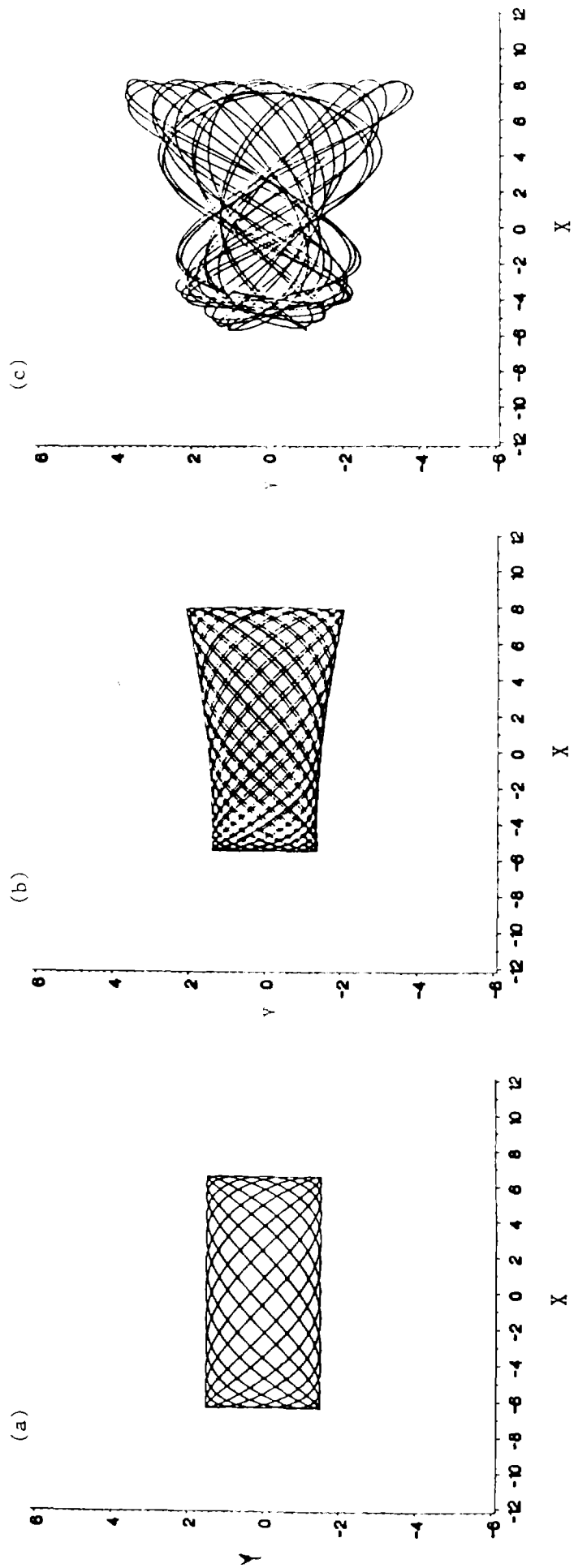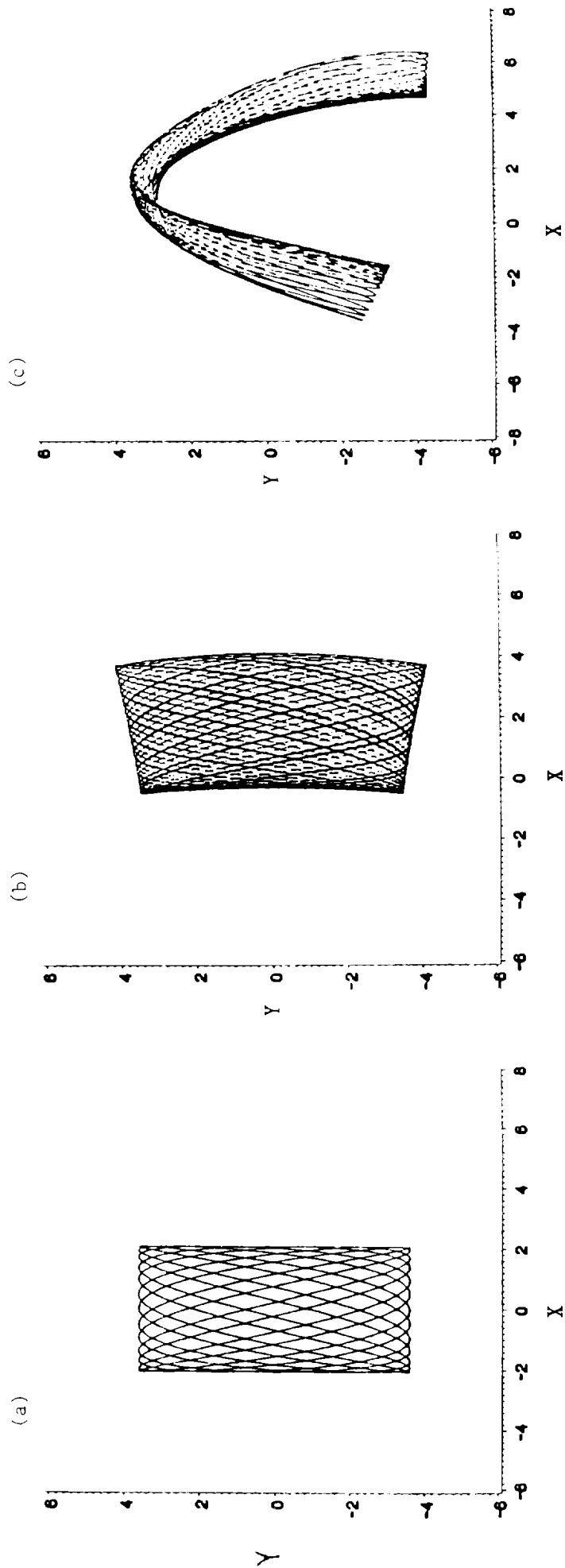
Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

(c)

Figure 7

(a)

(b)

(c)

Figure 8

-33-